Safety Considerations of Ozone Buildup in the MECO PS LN$_2$ System

This is to discuss the possible effects of ozone production in the nitrogen heat shield. The potential problem was first pointed out to us by Wuzheng Meng, for which we are grateful. The concern is that ozone will collect and, when warmed, revert to O$_2$ in an exothermic reaction that would release significant energy into the LN2 lines that trace the thermal shields. The concern is discussed in the paper of C.R. Gregory and C.W. Nuttall, CERN AT/95-06 (DI), attached as Appendix A.

In discussing some explosion accidents in cryogenics systems, the paper states "It soon became clear that significant quantities of ozone (O$_3$) were being produced during the irradiation of material samples and that the ozone generation was due to the action of ionizing radiation on the relatively small quantities of dissolved oxygen present in the liquid nitrogen. It appears that shock, local heating or even the presence of solid organic resins such as epoxies can trigger this type of explosion."

Of course, our system is not identical to systems described or referenced in the paper of Gregory and Nuttall. Understanding how our system would react depends on knowing the properties of ozone and its interaction with LN$_2$. Much information on ozone properties is given in Streng, Journal of Chemical and Engineering Data 6, 1961 (431), attached as appendix B.

Since explosion is a frightening word, it is useful to put this in perspective. First, we note that the explosions referred to only occurred when the ozone concentration in the LN$_2$ exceeded 4%; as we discuss below, the concentration in the MECO system under any of a number of possible operating scenarios would never exceed 0.04%. Streng reports explosions below this (without details) and apparently only when the fluid is not well mixed and high concentration regions existed. As discussed below, we don't see any scenario in which this can occur in our system. Second, even if the ozone did somehow spontaneously revert to O$_2$, it is not a personnel safety hazard, or even an issue of damage to the cryostat, or even an issue of rupture of the LN$_2$ cooling tubes, but only an issue of possible deformation of the heat shield. This itself we cannot tolerate, since it would be a significant loss of it caused a thermal short necessitating repairs.

Relevant to the question at hand is the vapor pressure of the produced ozone and the solubility in nitrogen. Absent some interaction that binds the ozone to the liquid nitrogen, the ozone will exist above the liquid at its saturated vapor pressure at 77 K, reduced by the fractional concentration in the liquid. It will also exist in whatever gas bubbles are produced by the heat transferred from the heat shield to the liquid nitrogen. A paper by Hanson and Mauersberger (J. Chemical Physics 85, 1986 (4669)) gives measurements of the vapor pressure of liquid or solid ozone in the relevant temperature range. It follows the relationship log [P/(1 torr)] = 10.460 – 1021.6/T. The pressure at 77 K is about 2 mTorr. Most relevant to our situation is the solubility of ozone in liquid nitrogen; Streng reports the solubility to be in the range of 4-5% (molar), measured by a number of groups.

The rate of production of ozone in LN$_2$ depends on the concentration of O$_2$ and on the amount of energy deposited. In the range of concentration relevant to us, the rate is given by

$$R(e) = R_o e + (8,05 + 1.29 \log e).$$

R is the production rate in units of molecules per 100 eV of deposited energy, R_0 is the production rate in pure O_2 (12.9) and e is the fractional oxygen concentration. This gives typical yields of a few molecules per 100 eV for O_2 concentrations of 10-10,000 ppm. Commercial liquid nitrogen typically has an O_2 concentration of below 10 ppm. We would handle the LN_2 carefully to insure that excess oxygen is not dissolved in the nitrogen, for example by exposing the liquid to a volume of air in the storage dewar.

To give a sense of the size of the problem, consider a concentration of 10,000 ppm O_2, well above what we expect. With a radiation dose rate of 20 μW/gm, 10 kg of LN_2 exposed to that radiation, and 10^7 seconds of running, the total amount of ozone produced is 1.14 moles, about 50 grams. For O_2 concentration of 10 ppm, the amount produced is about half that. The energy released in converting $2O_3$ to $3O_2$ is 3000 J/gm.

We can imagine operating the LN_2 cooling system in a number of ways. In all of these, the nitrogen flows through relatively small cooling tubes that are attached to the thermal shield. Flow is maintained either by pumping or by convection. The typical velocity is about 10 cm/s, assuming cooling tubes with ID=0.5 cm.

1. Method 1 is to operate with a conventional liquid recycling system, venting the gas that is produced during the cooling process and replenishing the LN_2 from commercial tanks as it is evaporated. The oxygen concentration will increase by preferential vaporization of nitrogen. If the oxygen in the produced vapor is at the saturated vapor pressure of oxygen at 77 K, then the equilibrium oxygen concentration in the buffer volume will be higher than the oxygen concentration in the supplied gas by the ratio of the partial pressure of nitrogen to that of oxygen at the operating temperature. That will increase the equilibrium oxygen concentration in the liquid by about a factor of 4, since the saturated vapor pressure of oxygen at 77 K is about 200 Torr.

   Table 1 below is a spreadsheet that allows the calculation of the resulting ozone concentration assuming no ozone is evaporated. For example, if we have a 500 liter (400kg) storage buffer, irradiate a 10 kg mass at a radiation level of 20   W/gm, run for 10^7 s, and assume the production rate is 2.4 molecules per 100 eV (typical for oxygen concentration of 40 ppm or 4 times a delivered concentration of 10 ppm), we would develop a molar density of a small fraction of a percent in the fully mixed buffer volume. This is well below the saturated solubility of ozone in LN_2. Even if the 10 kg remains in the irradiated region, the ozone concentration is only about 0.14%, well below the level at which it would start to precipitate out as a solid. In fact, the LN_2 is well mixed because of the continuous circulation and we expect the lower concentration to apply.

Total mass [gm]	Irrad. mass [gm]	Rad. [J/s/gm]	ozone prod.rate [mol./eV]	Time [s]	ozone prod. rate [mole/s]	ozone prod. [moles]	ozone conc. [mole %]
4.0E+05	1.0E+04	2.0E-05	0.024	1.0E+07	5.0E-08	0.50	3.5E-03

Table 1. Spreadsheet showing the calculation of the amount of ozone produced in 10^7 running at full intensity.

   It is rather easy to monitor the ozone concentration in liquid by fully vaporizing a fraction of the liquid and passing it through an ozone monitor (basically an absorption spectrophotometer). At the end of the running, the ozone-contaminated liquid would be thrown away (vented into the parking lot) and clean LN2 flowed through the system. It could

then be verified that no ozone is present in the effluent, to ensure that the system is clean before it is warmed.

Ozone concentrations as small as a few ppm can be readily measured since it has a high absorption cross section for UV light.

2. Method 2 is to operate a totally closed re-circulating system (condensing the returned gas) so that the oxygen level (and hence the highest possible ozone level) can never get above the level in the delivered gas, far below the level at which ozone can condense. Here, we would eventually get to an ozone level of no more than the delivered concentration of oxygen, of order 10 PPM, far below the concentration necessary for it to precipitate out. Periodically, this LN_2 would be thrown away (vented into the parking lot). Again, the ozone concentration in the liquid could be monitored.

3. Method 3 is to operate with a single-pass system; this is the default operation. The cost of this option depends on what fraction of the LN_2 can be vaporized during the pass. Table 3 below is a spreadsheet that allows different assumptions to be tested. The cost of LN_2 is taken to be about $0.07 per liter. The heat load on the nitrogen system for the PS is about 130 W (it is significantly higher in the other magnets). Assuming the exit LN_2 flow has quality 0.5 (50% gas by mass), then the cost per day to vent all the LN_2 that is used to cool the PS is about $10, a negligible cost. In this scenario, the ozone concentration in the system is always negligible. Again, the ozone concentration in the vented nitrogen (gas plus liquid) could be monitored easily.

Nitrogen Flow	Power [J/s]	LN2 frac. vaporized	1/LHV [moles/J]	Flow [moles/s]	Flow [m3/s]	O3 prod. [mole/s]	Outlet Conc. [moles/m3]	cost [$/day]
	130	0.50	1.72E-04	4.47E-02	1.57E-06	6.20E-08	0.0396	9.74

Table 2. The table is a spreadsheet showing the cost of a single-pass option for running the LN_2 cooling system.

These three methods for operating the LN_2 cooling system in a safe way rely on two assumptions.

One assumption is that there is not a small, uncirculated volume of LN_2 in the highly irradiated area, in which a higher ozone concentration is built up, and that this region is not periodically flushed out, and that the ozone does not diffuse into neighboring regions. Hence, it is important to design the LN_2 distribution so that a stagnant region will not develop. Certainly most of the liquid that is irradiated must also be flowing. If not, that region of the magnet would not have its thermal heat shield cooled and the temperature of that region of the shield would increase, LN_2 would be vaporized, and either flow would start or the pressure would rise. It would seem to be difficult to design a system where signification stagnation could develop.

The second assumption is that there is not some anomalous adsorption of ozone on the tubing material. There is no evidence that we have been able to find that there is such adsorption on stainless steel. We can try to estimate how much might occur. Surface scientists with whom we have consulted state that once an adsorbed surface layer is more than a few (3-4) atomic layers thick, the surface has the characteristics of the bulk adsorbed material, and can then be treated as if the substrate has no effect. In that case, bulk solid ozone properties (including solubility in LN_2) would apply. Since the O_3 concentration in the liquid is always very far below the saturated concentration, it would no longer build up. For a very conservative estimate of the amount of ozone that might exist as an adsorbed layer, we assume a 35 Angstrom layer (8 molecules thick) that covers the interior of tubing with an ID of 0.5 cm, about 600 feet long (1 foot of tubing per square foot of heat shield). The calculation of the energy

release is given in the spreadsheet below; it is only about 80 Joules, even with the conservative assumptions above.

Density [gm/cm^3]	Atomic #	Avagaodro's number	Atomic Vol [cm^3]	Layer Thick. [Angstrom]
1	48	6.00E+23	8.00E-23	4.31

Calculation of thickness of atomic layer.

Length [feet]	ID [cm]	Thickness [cm]	Ozone Vol [cm^3]	Density [gm/cm^3]	Mass [gm]	Energy [J]
600	0.5	3.50E-07	0.026	1	0.026	78

Gas Vol [m^3]	Pressure [Pa]	R [J/K/mole]	T [K]	Moles	Temp Rise [K]	Press. Rise [Pa]	Press. Rise [PSI]
0.0046	100000	8.4	100	0.55	6.2	6181	0.91

Table 3. The table is a spreadsheet showing a calculation of the amount of ozone that might be adsorbed on the inner surface of the cooling tubing and the amount of energy released if it spontaneously converted to O_2. It also shows the pressure rise in the tubing assuming that the event occurred when the tubing was filled with gaseous nitrogen at 100 K and all the energy went into heating the nitrogen.

This would not be a damage hazard even if it converted to O_2 explosively. Table 3 shows the calculation of the pressure rise in the tubing system, assuming it is closed and filled with nitrogen at 100 K and atmospheric pressure when the event happened. Note that the increase in the number of gas molecules is negligible, since less than 0.001 moles of O_2 are produced, and the volume contains 0.55 moles of N_2.

We conclude that there is more than one way of operating the magnets safely with LN_2 cooling loops tracing the thermal radiation intercept. The default operation mode is simple and inexpensive.

EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Explosion Risks in Cryogenic Liquids Exposed to Ionising Radiation

C. R Gregory, C. W. Nuttall

Abstract

Explosions in cryogenic fluids were first reported in the early 1950's. Numerous papers have been presented describing these explosions and proposing mechanisms as to their cause. The majority of these incidents have occurred in dewars and cryogenic systems containing liquid nitrogen which have been exposed to ionizing radiation.

It is now widely accepted that the explosions are caused by the very rapid decomposition of ozone, which is formed by the action of ionising radiation on oxygen dissolved in liquid nitrogen.

There is also evidence that oxides of nitrogen are formed and although it is not suggested that these compounds are the primary cause of explosions they do seem to play a catalytic role in the formation of ozone, as indeed they do in the formation of ozone in atmospheric reactions.

This paper is aimed at drawing the attention of designers of cryogenic systems in the LHC areas to the problem, in order that precautions can be taken at the design stage to reduce, or eliminate, the dangers of such explosions.

CONTENTS

1   INTRODUCTION

Cryogenic fluids such as *Liquid Nitrogen , Argon and Helium* have been used for many years to provide low temperature environments for experimental and other purposes because they are inert, non flammable, non toxic and generally regarded as posing little hazard.

However under certain conditions explosions [1, 2, 3] have occurred, including some at CERN, notably in liquid nitrogen systems, after exposure to ionising radiation, for which, at the time, there was no explanation. Explosions have occurred in cryostats that have been subjected to doses of gamma radiation in the order of 10^4 Gy[4] , neutron fluxes of 10^{12} n.cm^{-2} sec^{-1}. for a matter of two to three hours[5], and irradiation by a beam of 20 μA of 2.0 MeV electrons for 4 minutes[3].

Radiation levels in the proposed LHC experimental areas will be much higher than those reached in existing LEP areas with projected integrated doses in the order of 2,3 . 10^5 Gy.yr^{-1}, and neutron fluxes of 10^9 n.cm^{-2}.sec^{-1} [6]. These values give cause for concern, particularly in the case of gamma radiation, as they are of the same magnitude as those reported in the literature where explosions have occurred.

The mechanisms of these explosions are very complex and are not yet fully understood. In this paper we review the existing literature on the subject and suggest precautions that may be required, or, further work that may be necessary to minimize explosion hazards in the LHC. Other explosions in liquefied gas containers have been caused by overpressure coupled with insufficient pressure relief, "roll-over" of the contents, or superheating resulting in the eventual catastrophic boiling of the contents. It is not intended in this paper to treat these phenomena as they are common to all cryogenic systems and are accounted for (or should be) in the design of all CERN systems.

2   HISTORIC

It might be supposed that chemical reactivity ceases at temperatures below about 100 K , but, on the contrary, many significant chemical syntheses have been described in which some operation requiring cryogenic temperatures forms a vital part of the procedure [7] .

The study of chemical reactivity at cryogenic temperatures is not new, the first experiments being reported at the end of the last century, when these fluids became available in sufficiently large quantities.

Large scale use of cryogenic fluids began in the early 1950's with the advent of the space and nuclear industries, their low cost and widespread availability has seen a multitude of uses in many fields.

3   EXPLOSIONS

As more research work was carried out, during the 1950's, into the effects of radiation on materials at cryogenic temperatures, explosions were reported for which there were no apparent explanations[3,5,8,9]. At first it was thought that the cryostat exhausts had become blocked by the formation of ice or as a result of design or operational errors, but it gradually became clear that some form of radiochemical reaction was taking place.

Liquid nitrogen was mainly used as the cooling media for these experiments, and therefore attention became focused on the possible contaminants. Commercial liquid nitrogen when delivered is usually relatively pure, however, it may easily become contaminated if it is allowed to come into contact with air. Due to their higher boiling points, oxygen and water vapour from the air are condensed and become dissolved in the liquid nitrogen.

It soon became clear that significant quantities of ozone (O_3) were being produced during the irradiation of material samples and that the ozone generation was due to the action of ionizing radiation on the relatively small quantities of dissolved oxygen present in the liquid nitrogen.

The generation of ozone during the operation of an experiment is of special interest not only because of the relatively high yields of ozone which are produced when oxygen is subjected to irradiation, but in particular due to the toxic and explosive properties of the gas.

As well as the production of ozone the irradiation of liquid nitrogen may also result in the formation of oxides of nitrogen (N_2O, NO, NO_2, N_2O_4 and N_2O_5) [10,11] and indeed the presence of a "sludge" of oxides of nitrogen has been reported at the bottom of liquid nitrogen cryostats after irradiation[4]. It is considered that the oxides of nitrogen are not the cause of the explosions but they seem to enhance the yield of ozone by a catalytic effect.

It has been suggested that "active" nitrogen, consisting of atoms and excited molecules of nitrogen, may be formed and be responsible for the explosions, but this is thought unlikely as it is so reactive that the molecules will not accumulate.

Violent explosions have occurred in experiments being conducted in cryostats of liquid nitrogen, and also in small, open glass vessels containing only milligram quantities of ozone. Sufficient explosive power is generated to shatter the internal components of cryostats or cryogenic containers. It appears that shock, local heating or even the presence of solid organic resins such as epoxies can trigger this type of explosion.

4   PHYSICAL PROPERTIES OF CRYOGENIC FLUIDS

4.1   General

The physical properties of the principal inert cryogenic fluids, together with those of oxygen, ozone and the principal oxides of nitrogen are given in Table 1.

FLUID	Boiling Pt. K (@1 atm.)	Melting Pt. K (@1 atm.)
Nitrogen (N_2)	77.35	63
Argon (Ar)	87.29	83.2
Helium (He)	4.22	-
Oxygen (O_2)	90.18	54.75
Ozone (O_3)	161.3	80.7
Nitrous Oxide (N_2O)	182.3	170.7
Nitric Oxide (NO)	122	112
Nitrogen Dioxide (NO_2/N_2O_4)	294.3	263.7
Nitrogen Pentoxide (N_2O_5)	320	303

Table 1: Boiling and melting points of liquefied gases

Since liquid oxygen is less volatile than either liquid nitrogen or argon, oxygen enrichment occurs as the liquid nitrogen boils off. If the cryostat is refilled before all the nitrogen has been allowed to boil off, then any condensed oxygen will remain. This is even more pronounced in the case of ozone. Therefore any ozone absorbed in either liquid nitrogen or argon will remain in solution as a dissolved solid.

Liquid oxygen and ozone have a pronounced blue colour and this colour has been reported by many workers in liquid nitrogen after irradiation.

At ambient temperature ozone is known to be unstable, it decomposes spontaneously if only relatively slowly. However the rate of decomposition is increased by the catalytic action of certain metals, the presence of other gases (e.g. NO), or by ionising radiation.

At temperatures below 90 K ozone is stable and does not decompose spontaneously, but under certain conditions it can decompose with explosive violence.

Explosions occur as ozone is rapidly reduced to oxygen (at a lower energy state) i.e. forming oxygen and releasing a large quantity of energy[12].

$$O_3 \rightarrow 3/2 \ O_2$$
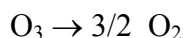
$$\Delta H = -3 \ kJ.g^{-1}$$

This energy of explosion, or decomposition, is similar to the experimental value for the energy of explosion of TNT which has been measured as 4.686 $kJ.g^{-1}$ [13]. Also the speed of detonation of pure ozone and TNT are very similar, at about 6000 $m.s^{-1}$.

4.2   Critical Explosive Concentrations

Chen et al.[5] postulate that the concentration of ozone needs to reach some critical value before explosions can take place. Cook et al.[14] state that phase separation occurs giving a layer rich in ozone which enhances the probability of explosion.

Streng[15] found that this phase separation is dependent not only upon the concentration, but also upon the temperature of the mixture of O_2/O_3, N_2/O_3 or Ar/O_3. Experimental work carried out by the French "Commissariat a 1'energie atomique (CEA)" [16] confirms this earlier work, but explosions have been observed in Ar/O_3 mixtures at ozone concentrations below the values proposed by Streng.

	Temperature K	Theoretical min.O_3 concentration Mole % (Streng)	O_3 Concentration Mole % at which explosion occurred (CEA)
Oxygen	78.4	6.3	6.4
Nitrogen	77.0	4.4	5.8
Argon	85.0	8.3	4.9

Table 2: Ozone concentrations required to cause explosion

5   OZONE FORMATION

The amount of ozone formed in liquid nitrogen - oxygen mixtures exposed to ionising radiation was measured by Riley[17]. and later by Gault[18]. It was found that G(e), the number of ozone molecules formed per 100 eV, could be expressed as

$$G(e) = Goe + (8,05 + 1,29\log e)$$

This is valid for oxygen concentrations in the range 52 - 8,75. 10^4 ppm, where Go is the ozone yield, 12.5 molecules/100eV, from pure oxygen at 77 K, and shows that ozone production is relatively efficient even for low oxygen concentrations. For example, ozone formation in liquid nitrogen containing 10^4 ppm oxygen, 5.7 molecules/ 100eV, is only 2.2 times that found in nitrogen containing 52ppm oxygen, 2.6 molecules/ 100eV.

The formation of ozone in liquid argon is thought to be similar to that of liquid nitrogen , but to date little concrete work has been carried out to verify this.

Experiments by Sears J. T. et a1.[19], suggest that the formation of ozone is dependent on dose at low doses but independent of dose rate, however, the steady state concentration of ozone was dependent on dose rate. This is also suggested in a theoretical study carried out by Brereton12. Impurities also play a complex role and can radically affect the steady-state yield of ozone.

Table 3, gives the concentrations of ozone and oxides of nitrogen formed in various technical and liquefied gases on irradiation as found by Dmitriev [20]. The impurity concentrations (O_2?) of the inert gases was assumed to be 0.5%.

Irradiated medium	O_3 concentration at $E = 10^4$ Gy. $(mg.m^{-3})$	NO_2 concentration at $E = 10^4$ Gy . $(mg .m^{-3})$
Gaseous Oxygen	$9.40 .10^2$	9.7
Liquid Oxygen	$2.7 .10^5$	$2.28 .10^3$
Air	$4.02 .10^2$	$2.90 .10^2$
Liquid Air	$1.5 .10^5$	$5 .10^4$
Gaseous Nitrogen	45	11
Liquid Nitrogen	$1.65 .10^3$	$1.17 .10^3$
Argon	$1.34 .10^2$	$1.05 .10^{-1}$
Helium	8	$1.3.10^{-2}$

Table 3. Ozone formation in technical & liquefied gases

It is evident from table 3 that the ozone produced when liquefied gases are irradiated is of the order 100 times more than for the same gases at ambient temperatures and that oxides of nitrogen are formed, albeit in much smaller concentrations than ozone. Nevertheless oxides of nitrogen may play an important role in the reactions leading to the formation of ozone.

6. CRYOSTAT CONSTRUCTION

A number of reports in the literature suggest that the materials used in the construction of the cryostats play an important role in the formation of ozone and that this formation must be, at least in part, due to surface reactions.

Work carried out by Douglas J. E. et a1. [21] , show that the production of ozone can be dependent on the material in contact with the fluid in the cryostat.

Unsaturated organic compounds react with ozone to produce ozonides, which are subject to sudden decomposition[22], and as araldite and polystyrene, which both contain double bonds, are known to play important catalytic roles in the decomposition of ozone[4], this may be due to the formation of ozonides. Careful consideration should be given to their employment, and that of similar compounds, in cryostats.

Ozone may concentrate at the interface of the liquid surface and the vessel wall due to the preferential evaporation of the liquid nitrogen. It is important to chose materials with low wetting properties to limit this phenomena.

7.   **REMOVAL OF OZONE**

Catalytic decomposition, or removal of ozone has been studied at ambient temperatures, but little work has been carried out into these processes at cryogenic temperatures.

Studies by d'Emel' Yanova et al [23,24] and Dewanckel et al.[25], into the catalytic decomposition of ozone in solution, in either liquid oxygen or nitrogen, indicate that platinum, palladium and to a lesser extent silver and copper are efficient at reducing ozone to oxygen. Certain metal oxides may also be employed to destroy ozone.

Activated carbon has a high adsorptive capacity for ozone even from dilute solutions, but this should not be considered as there is a risk of accumulating relatively large quantities of ozone, with the consequent risk of explosion when warming up the system.

8.   **DISCUSSION**

It has been shown at CERN, and at other places, that explosions in cryogenic liquids can occur when these are exposed to ionising radiation. This radiation may be gamma rays, electrons or neutrons. The cryogenic liquid in which most explosions have taken place has been liquid nitrogen, with a few in liquid argon. The mechanism for the explosions is almost certainly the explosive decomposition of ozone, initiated by shock, or by the presence of polymeric materials in the construction of the cryostat or the presence of foreign matter such as dust particles acting as catalysts. The ozone is formed by the irradiation of oxygen impurities dissolved in the cryogenic liquid. There is some evidence that nitrogen plays a role in the reactions leading to the formation of ozone, but the preponderance of explosions in liquid nitrogen systems may simply be due to the fact that many more liquid nitrogen systems have been exposed to ionising radiation than have, for instance, liquid argon systems.

The quantity of ozone formed is a function of the total dose and very much less a function of the initial oxygen content. The effect of the dose rate is less clearly understood.

The above mechanism appears to represent a serious risk to the cryogenic systems being proposed for the LHC experiments, since quantities of cryogenic liquids will be found in zones of high radiation (e.g. EM Calorimeter end caps). The total annual dose will fall within the range known to create dangerous amounts of ozone in liquid nitrogen, or, argon and the complexity of the system could well facilitate the contamination of the cryogens by oxygen unless special precautions are taken.

It is of primary importance that these problems be addressed at the design stage, to reduce the potential danger by minimising the quantity of oxygen within the radiation field, for example using closed cycle secondary circuits filled with pure liquids cooled by heat exchange with commercial liquid nitrogen not exposed to ionising radiation.

It would be wise to monitor continuously the oxygen level in the cryogens exposed to ionising radiation and it may be necessary to design in systems for the removal of ozone as it is formed should the studies show that the risk to the cryogenic systems in the LHC experiments is such that it cannot be accepted.

This report has concentrated on the experimental areas where liquid nitrogen and argon will be present, for it is in these systems that most explosions have occurred. As far as we are aware there have

been no reported incidents due to the problem of ozone formation and explosive decomposition in irradiated liquid helium. However there have been reports of ozone formation and explosion in solid air condensed on external cold sots of liquid helium cryogenic systems exposed to ionising radiation[27]. This problem should be taken into account in the design and operation of the cryogenic systems of the LHC machine.

As stated above, the total dose plays an important role in the formation of ozone, although the effects of dose rate and oxygen concentration are less clearly defined. The role played by nitrogen oxides in the formation of ozone is also unclear, as although these compounds do not appear to be the source of explosions, they may catalyse the formation of ozone. Further experimental work into the effects of dose rates and oxygen concentration would be of great value, as would work on the risks in liquid argon systems as much less information exists on this latter subject.

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